# Evaporative Evolution of Brines from Synthetic Topopah Spring Tuff Pore Water, Yucca Mountain, NV

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## Abstract

We are investigating the evaporation of pore water representative of the designated high-level-nuclear-waste repository at Yucca Mountain, NV to predict the range of brine compositions that may contact waste containers. These brines could form potentially corrosive thin films on the containers and impact their long-term integrity. Here we report the geochemistry of a relatively complex synthetic Topopah Spring Tuff pore water that was progressively evaporated in a series of experiments. The experiments were conducted in a closed vessel, heated to 95°C, and purged with atmospheric $CO_2$. Aqueous samples of the evaporating solution were taken and analyzed to determine the evolving water chemistry, and the final solid precipitate was analyzed by X-ray diffraction.

The synthetic Topopah Spring Tuff water evolved towards a complex brine that contains about 3 mol% $SO_4$, and 2 mol% Ca, 3 mol% K, 5 mol% $NO_3$, 40 mol% Cl, and 47 mol% Na. Trends in the solution data and identification of $CaSO_4$ solids (anhydrite and bassanite) suggest that fluorite, carbonate, sulfate, and Mg-silicate precipitation minimize the corrosion potential of "sulfate type pore water" by removing F, Ca, and Mg during the early stages of evaporation

## Introduction

Evaporative concentration experiments reported here investigate the evolution of the pore water found in rock formations within (Topopah Spring Tuff) and above (Paintbrush) the designated high-level-nuclear-waste repository at Yucca Mountain, NV. The primary goal of our experiments is to provide constraints on water chemistries and salt compositions that are likely to contact and react with the high-level waste canisters and any engineered canister shields. Once completed, our experimental work will also provide much needed data to test and validate the development of Pitzer data base and geochemical codes used by the Engineered Barrier System and the Unsaturated Zone to model the long-term performance of the repository.

The measured compositions of Yucca Mountain pore water vary, but can be generally placed into three types of waters that should evolve towards specific brine chemistry as the waters evaporate as the repository heats up (Figure 1):

1. Carbonate brine with alkaline pH      Na-$CO_3$-Cl-$SO_4$
2. Sulfate brine with near neutral pH      Na-Mg-Cl-$SO_4$
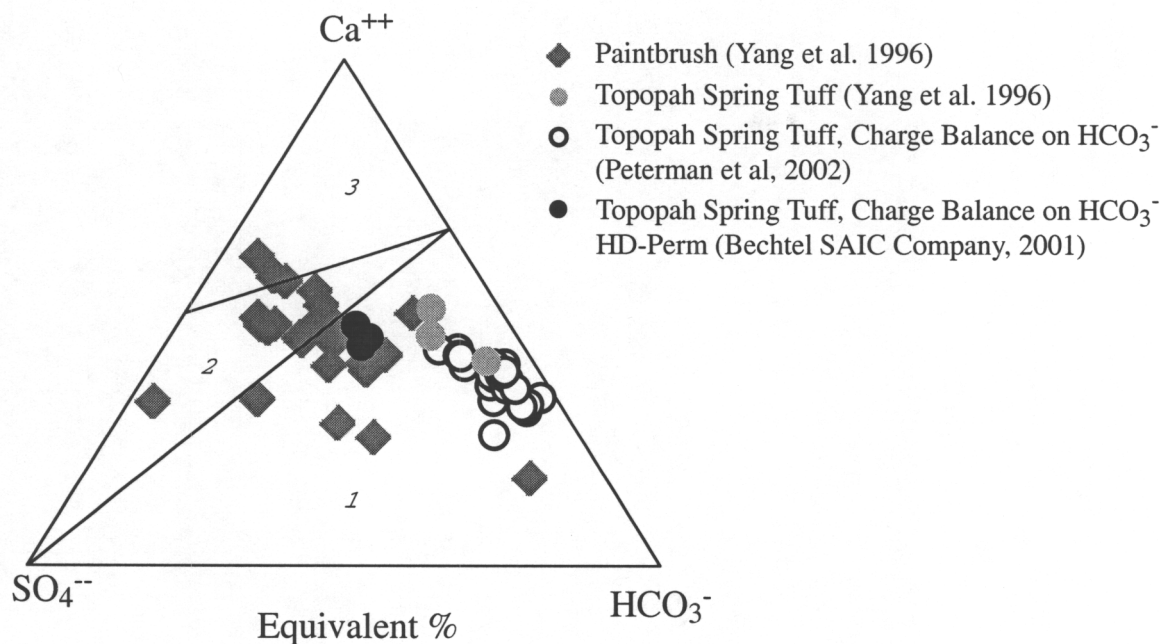3. Ca-chloride brine with near neutral pH    Na-Ca-Mg-Cl

**Figure 1**. Yucca Mountain pore waters as measured by Peterman and Yang (equivalent %).

Of concern to the Yucca Mountain Program, is that some of these pore waters could evolve to potentially corrosive $CaCl_2$, $MgCl_2$, and fluoride brines as well as the more benign carbonate and sulfate brines. The simple ratios of Ca, $SO_4$ and $HCO_3$ in Figure 1 illustrate the dominant carbonate and sulfate chemical divides that occur as waters evaporate (Eugster and Hardie, 1970; Eugster and Hardie, 1978, Li et al., 1997), but Figure 1 does not show important chemical divides for Mg, Si, or F. Nor does is show the relative magnitude of these salts to other major ions such as $NO_3^-$, which have shown to inhibit corrosion in mixed chloride-nitrate solutions (Brossia and Kelly, 1998). Temperature will also impact the evolution of the pore water. Recent modeling of Yucca Mountain pore water within the carbonate brine field at 25°C, evolved towards potentially corrosive Ca-chloride brines at 95°C, and not towards a more benign carbonate brine as predicted by Figure 1 (Bechtel SAIC Company, 2001).

Here we report our results for the evaporation of a synthetic Topopah Spring Tuff pore water at 95°C over a concentration range of 1x to ~400x.

**Experimental Methods**
Table 1 shows the chemical composition of the synthetic Topopah Spring Tuff pore water that was evaporated in three legs of this experiment. The chemical composition of the second leg was based on the brine composition towards the end of the first leg, and the composition of the third leg was based on the brine composition towards the end of the second leg. The solutions were prepared using analytical grade salts. Evaporation was conducted in a vented vessel heated to 95°C, and purged with atmospheric $CO_2$. The

extent of evaporation was monitored from the condensed water vapor vented from the reaction vessel. Periodic samples of the evaporating solution were filtered and analyzed

**Table 1** Starting compositions for the evaporation of a synthetic Topopah Spring Tuff pore water.

|  | Leg 1 (Exp. FEC 9) molal 25°C | Leg 1 (Exp. FEC 9) molal 95°C | Leg 2 (Exp. FEC 12) molal 95°C | Leg 3 (Exp. FEC 13) molal 95°C |
|---|---|---|---|---|
| F | $5.95 \times 10^{-5}$ | | | |
| $K^+$ | $1.76 \times 10^{-4}$ | $1.63 \times 10^{-4}$ | $5.81 \times 10^{-4}$ | $6.47 \times 10^{-3}$ |
| $NO_3^-$ | $3.53 \times 10^{-4}$ | $3.94 \times 10^{-4}$ | $1.32 \times 10^{-3}$ | $1.17 \times 10^{-2}$ |
| $Mg^{++}$ | $1.01 \times 10^{-3}$ | $6.48 \times 10^{-4}$ | $6.04 \times 10^{-4}$ | $1.05 \times 10^{-3}$ |
| $SO_4^{--}$ | $1.23 \times 10^{-3}$ | $1.85 \times 10^{-3}$ | $4.64 \times 10^{-3}$ | $2.22 \times 10^{-2}$ |
| $SiO_2$ | $1.39 \times 10^{-3}$ | $9.21 \times 10^{-4}$ | $1.98 \times 10^{-3}$ | $2.22 \times 10^{-3}$ |
| $Ca^{++}$ | $1.57 \times 10^{-3}$ | $1.25 \times 10^{-3}$ | $4.68 \times 10^{-3}$ | $2.15 \times 10^{-2}$ |
| $Na^+$ | $2.84 \times 10^{-3}$ | $3.04 \times 10^{-3}$ | $1.10 \times 10^{-2}$ | $1.10 \times 10^{-1}$ |
| $HCO_3$ | $7.93 \times 10^{-4}$ | $3.11 \times 10^{-4}$ | $1.59 \times 10^{-4}$ | not analyzed |
| $Cl^-$ | $3.26 \times 10^{-3}$ | $3.31 \times 10^{-3}$ | $9.79 \times 10^{-3}$ | $1.04 \times 10^{-1}$ |

to determine the evolving water chemistry. pH was measured at room temperature with a combination electrode, total dissolved carbon was measured with an infrared carbon analyzer, dissolved Ca, Mg, Si, and Na were measured with an inductively coupled plasma-atomic emission spectrometer, and dissolved K was measured using an atomic absorption spectrophotometer, and F, Cl, $NO_3$, and $SO_4$ anions were determined using ion chromatography. The solid precipitate was collected at the end of each leg of the experiment and analyzed by X-ray diffraction.

**Results and Discussion**

Our experimental results are summarized in Figures 2 and 3. The pore water composition appears to be controlled by the precipitation of a small amount of calcite removing all measurable dissolved $CO_2$ and the precipitation of anhydrite ($CaSO_4$) and/or bassanite ($2CaSO_4 \bullet H_2O$). These are the dominant chemical reactions predicted by chemical divide theory, which forms the basis for the $Ca:HCO_3:SO_4$ diagrams in Figures 1 and 2. Figure 2 shows the evolution of the water as it evaporated. The pore water evolved towards a $SO_4$ brine as predicted by chemical divide theory based on its initial $Ca:SO_4:HCO_3$ ratio. At the conclusion of the third leg (400x), the water composition had evolved to molar $Ca:SO_4 = 42:58$. It is important to note that sulfate concentrations will be minor compared to the concentration of Na, Cl, and $NO_3$ which have not be removed by mineral precipitation. At the conclusion of the third leg of this experiment, molar equivalents of Na and Cl were much greater than that of Ca and $SO_4$ ($Na:K:Ca:Cl:SO_4:NO_3 = 47:3:2:40:3:5$). Figure 2 also shows that a J-13 well water and a different Yucca Mountain unsaturated zone pore water (Rosenberg et al., 2001) evolve towards their respective Na-carbonate and Ca-chloride brines indicated by their initial $Ca:SO_4:HCO_3$ ratios. Although our results coupled with previous evaporation experiments (Rosenberg et al., 2001) suggest that $Ca:SO_4:HCO_3$ ternary diagrams can be used as a rough prediction of brines formed from dilute Yucca Mountain pore water, they do not capture

all of the important chemical divides that could affect the evolution of Yucca Mountain pore water such as fluorite and Mg-Silicate precipitation.
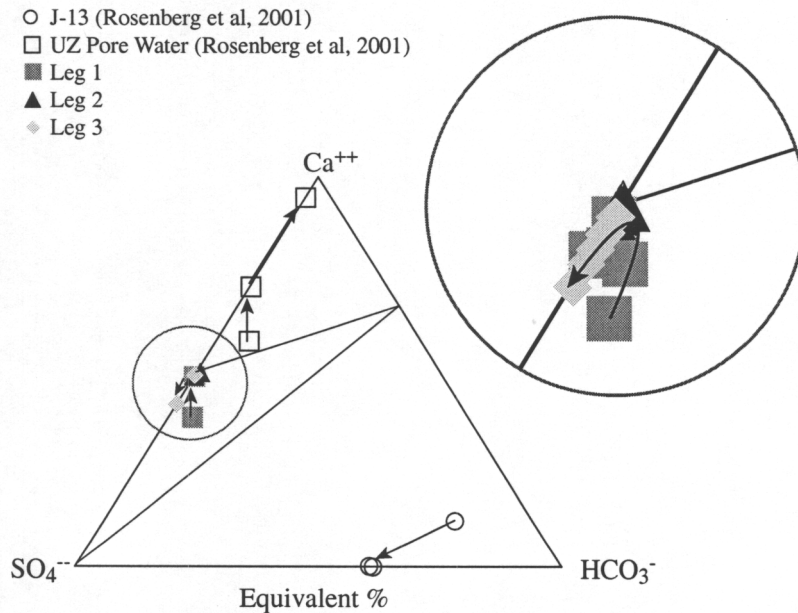


**Figure 2.** Evolution of a synthetic Topopah Spring Tuff pore water.

Figure 3 shows the evolution of the solution composition for all of the major elements comparing their relative concentrations to the concentration factor. The concentration factor is directly calculated from the amount of condensed water vapor during the evaporation experiment. Elements exhibit conservative concentration if they plot on the 1:1 correlation line and they exhibit removal by mineral precipitation if they plot below this line. The error bars in Figure 3 represent a 10% experimental uncertainty that reflects difficulties in synthesizing the "exact" solution composition from the end of one leg of the experiment to the beginning of the next leg. Figure 3 clearly shows the removal of Si, Ca, Mg, and $SO_4$. Amorphous silica precipitation and a Mg-silicate phase most likely controls the dissolved Si and Mg concentrations, which formed in the initial solution for leg 3. Dissolved $SO_4$ and Ca concentrations are controlled by sulfate precipitation as bassanite and/or anhydrite, which were identified in the X-ray diffraction patterns. In agreement with our results, Hardie and Eugster (1970) reported calcite, sepiolite ($Mg_8H_6Si_{12}O_{30}(OH)_{10} \cdot 6H_2O$), and gypsum($Ca_2SO_4 \cdot 2H_2O$) as early precipitates in saline lakes. The precipitation of both Mg and Ca as sulfate and/or silicates are important geochemical controls that will minimize the relative proportion of potentially corrosive Mg-chloride and Ca-chloride brines. The initial solution contained trace amounts of F which were rapidly removed from solution (data not shown) presumably as highly insoluble fluorite ($CaF_2$). This is an important geochemical control for F, a highly corrosive anion, and suggests that it will not threaten the integrity of the waste canisters or the drip shields in the repository. Figure 3b also suggests that there is some

precipitation of Cl and $NO_3$ above the predicted uncertainty. This mostly likely represents evaporation along the vessel walls as the water level drops, and the
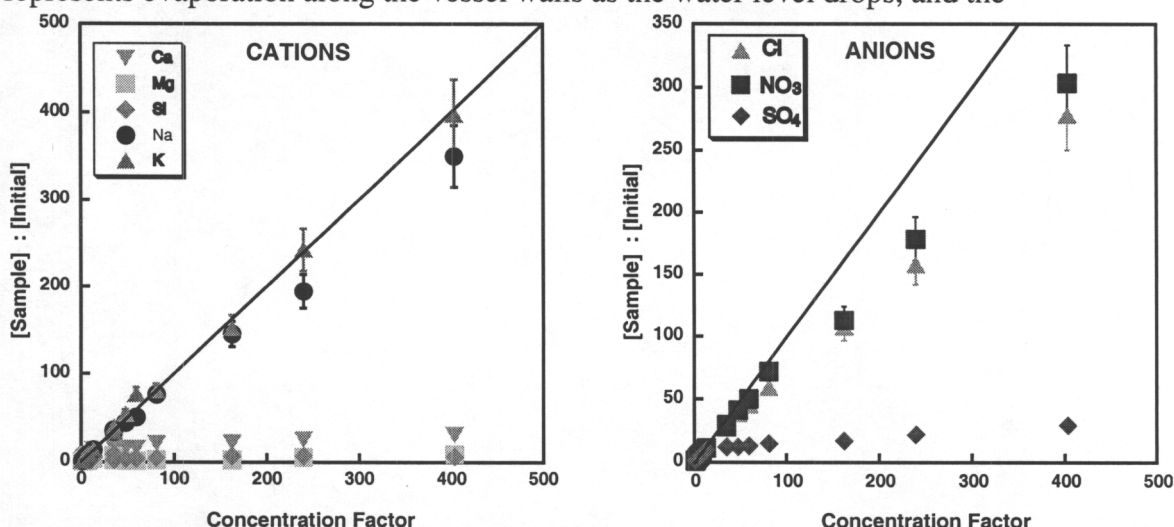


**Figure 3.** Evolution of a synthetic Topopah Spring pore water plotted as measured sample:initial concentrations versus the concentration factor (see text for additional explanation).

experimental uncertainty reflecting the difficulty in synthesizing the exact solution from one leg to the other.

## Conclusions

Our work shows that fluorite, carbonate, sulfate, and Mg-silicate precipitation minimize the corrosion potential of "sulfate type pore water" by removing F, Ca, and Mg during the early stages of evaporation, yielding a Na-K-Cl-$SO_4$-$NO_3$ brine. Future work includes continued evaporation of this water and other sulfate, calcium chloride, and carbonate waters indicated in Figure 1 from 1 X to 10,000 X to determine Yucca Mountain pore water evolution during evaporation and to test the Pitzer data base and geochemical models.

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